Synthesis of 3,5-Anhydro-2-deoxy-1,4-glyconolactones by Palladium(II)-Catalyzed, Regioselective Oxycarbonylation of C_5- and C_6-Enitols. ω-Homologation of Aldoses to Produce Intermediates for *C*-Glycoside/*C*-Nucleoside Synthesis[1]

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Dedicated to Prof H. J. Bestmann

The palladium(II)-catalyzed oxycarbonylation, known with alkenols and alkenediols, is studied with optically active 4-pentenitols (-triols) **1**, **7** and 5-hexenitols (-tetrols) **12**, **15**, **18**. Efficient routes for the substrates are provided, mostly from carbohydrate precursors. In all cases, bicyclic 3,6-anhydro-2-deoxy-1,4-glyconolactones, versatile intermediates of *C*-glycosidic structure, are isolated with high selectivity and in good yield (53–77%). Several minor products (4–14% of regio-/diastereoisomers) from two competing pathways are observed and identified. The oxycarbonylation of alkenitols thus completes a novel sequence that transforms aldoses into homologous anhydro-glyconolactones, by C_1-elongation at the terminal site. In the key step, the 3,4-threo arrangement is produced, from each of the four diastereomeric alkenitols studied (of the 6 cases available in the C_5 and C_6 series). The stereochemical protocol is summarized, e.g., by the transition D-*gluco* (aldose) → D-*xylo* (hexenitol, **15**) → L-*ido* (anhydro-deoxy-heptenolactone **26**), as demonstrated.

The homologation of monosaccharides has received much attention since many 'higher' carbohydrates, up to C_{11}, are known, and mostly show significant physiological activity.[2] Furanosidic or pyranosidic derivatives of such higher carbon sugars, natural or unnatural, are also represented by, or may be viewed as, intermediates for syntheses of *C*-glycosides,[3,4] *C*-disaccharides,[5] *C*-nucleosides,[3,4] or substituted tetrahydrofurans present in many ionophore antibiotics.[6] Approaches to elongate the carbon skeleton of carbohydrates or derived material by functionalized *C*-units inevitably face problems of selectivity, i.e., of chemo-, regio- and/or stereo-differentiation. Of these, (i) to suitably arrange the mandatory pattern of temporarily deactivating, "protecting" groups for the respective substrate, and (ii), to establish the proper configuration at the 'anomeric' centre of the *C*-glycosidic product, have remained a challenge, despite many respective efforts and several promising advances.[7–13]

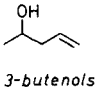
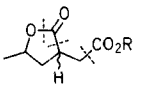
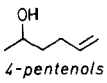
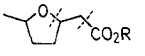
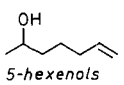
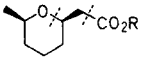
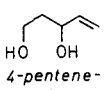
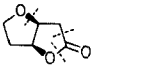
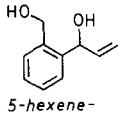
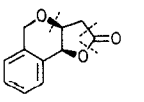
We present here a new, general approach to optically active anhydroalditols,[14–18] a class of compounds that have proven most versatile intermediates for such syntheses.[14,15] Our entry into this field features the palladium(II)-catalyzed oxycarbonylation of *unprotected* enitols as a key step. It is based on findings by Tamaru, Yoshida and co-workers, with respective reactions of 3-butenols and 3-pentene-1,3-diols,[19,20] and by Semmelhack et al. with 4-pentenols,[21,22] 5-hexenols, and 5-hexene-1,4-diols.[23] Each one of these shows its own, peculiar mode of regioselective CO incorporation, with stereoselectivities ranging from high to negligible, see Table 1.[24–29]

Optically active 5-hexenitols, i.e. 5-hexene-1,2,3,4-tetrols, comprise *all* of these structural features. In submitting such substrates to the Pd(II)/CO system, the main question therefore is if one of the above pathways would take precedence of the others to a preparatively useful extent. Since the regio- and diastereo-differentiation might be governed by the configuration of the ene-polyol substrate, this second aspect was to be addressed by securing and employing different C_5- and C_6-enitol diastereomers.

Enitols represent a class of carbohydrate derivatives, that is readily available (*vide infra*) but has hardly found applications in synthesis. Previously, we have provided access to C_5 *erythro* compounds **1** and the like, both from carbohydrate (D-ribonolactone)[30–32] and achiral precursors (1,4-pentadien-3-ol, as a unique achiral substrate for asymmetric Sharpless epoxidation).[30,32,33] These studies were started in conjunction with questions related to the stereoselectivity of nitrile oxide cycloadditions[30,33] and to the design of superior amino/iminopolyol syntheses.[28,34,35]

The *threo* diasteromer **7**, required for the present study, was obtained via the Sharpless product **2** (*erythro*) likewise. Since **2** and its regio-/diastereomer **3** (*threo*) are available in either enantiomeric form,[30,32,33] *any* clean substitution at C-2 or C-3 by OH (or an equivalent *O*-nucleophile) with inversion in **2** or retention in **3**, would give access to one or the other enantiomer of the required *threo* isomer **7**. Four protocols to achieve this transform-

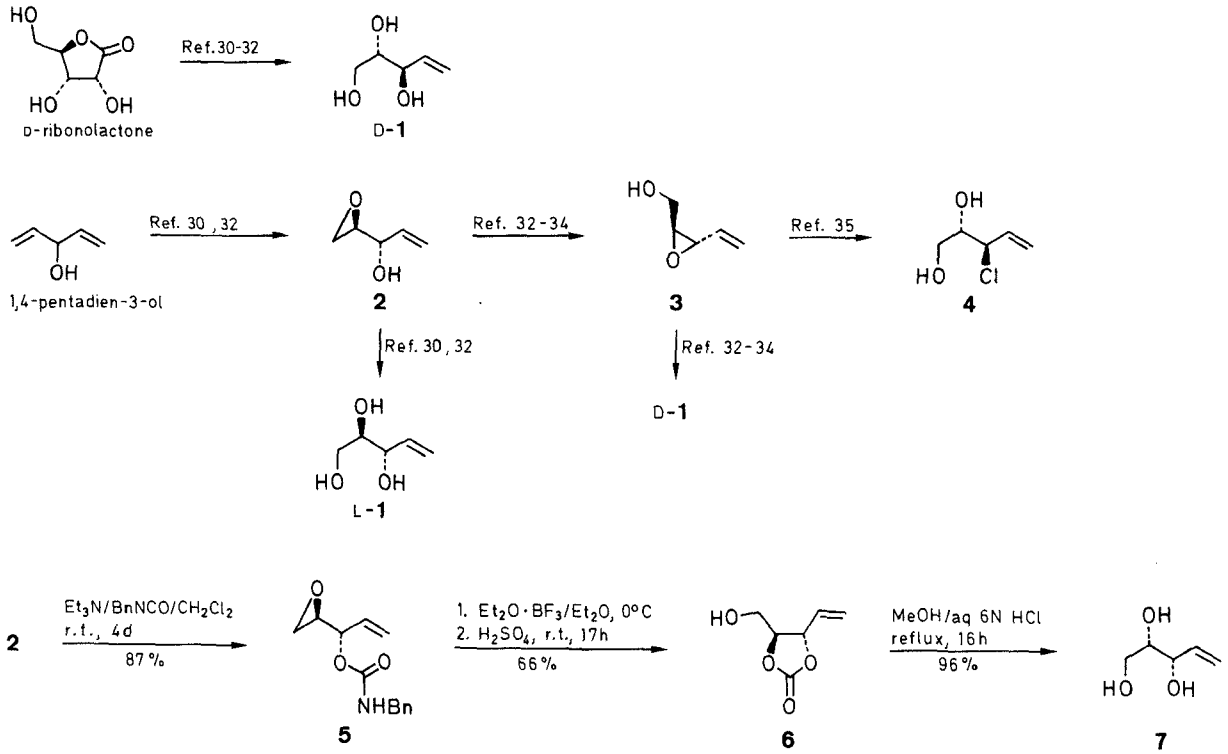
Table 1. Known Types of Pd(II)-Catalyzed Carbonylation of Alkenols

Substrate	Product(s)	Stereochemical Outcome	Ref.
 *3-butenols*		*cis* + *trans*	19, 20
 *4-pentenols*		*cis* + *trans*	21, 22
 *5-hexenols*		*cis*	23
 *4-pentene-1,3-diols*		*cis*[a]	19, 20
 *5-hexene-1,4-diols*		*cis*	23

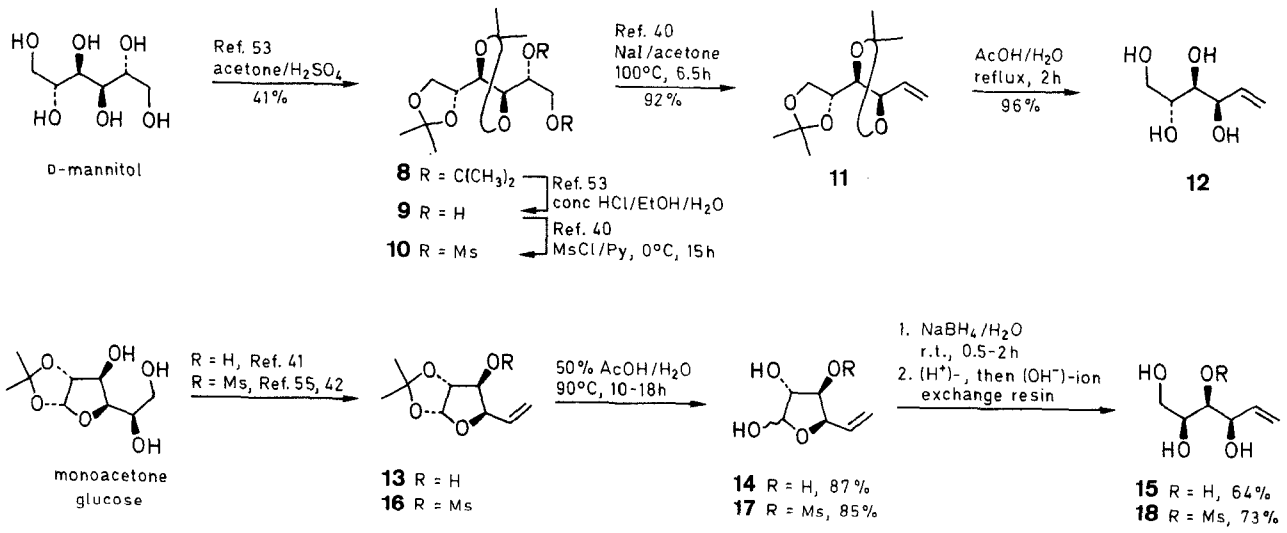
[a] Or 

ations were studied: (i) Trost's method, Pd(0)-catalyzed, stereoretentive carboxylation of vinyl-epoxides, successful with the 1-*O*-tosylate of **3** in Scharfs group;[36] (ii) carboxylation catalyzed by cesium carbonate, with inversion at C-2;[37] (iii) double inversion at C-3 of the internal epoxide **3**, first by chloride,[35] then by hydrolysis of **4**, as had been successful for the preparation of 3-amino-4-pentenediols;[35] (iv) inversion at C-2 via the epoxy-urethane **5** derived from **2**.[38,39] Of these, the latter method[39] proved the most satisfactory and gave the *threo*-triol **7**, after hydrolysis of the intermediate 2,3-carbonate **6**, in 55% yield from **2**, see Scheme **1**. The optical purity of **7** was expected to be ca. 96:4 (e.r.), as judged from capillary GC analysis of **1** reported earlier,[30,32] and assuming a uniform reaction course. Indeed, the specific rotation found for **7** compares very well with a previous estimate from a **1**/**7** mixture obtained from glyceraldehyde.[32]

The C_6 substrates, the hexenitols **12**, **15** and **18**, were prepared from D-mannitol and monoacetone D-glucose, adopting known routes to the protected olefinic intermediates **11**,[40] **13**,[41] and **16**,[42] see Scheme **2**. Hydrolysis for these cases was effected with aqueous acetic acid,[43] to afford the *lyxo*-hexenitol **12** and the unsaturated aldoses **14** and **17**. Sodium borohydride reduction of the latter went smoothly, although the removal of byproducts (borate) necessitated passage through acidic, then basic ion exchange resins.[44] The enitols **12**,[40,45] **15**[40] had been obtained previously by less efficient routes (cf.



Scheme 1



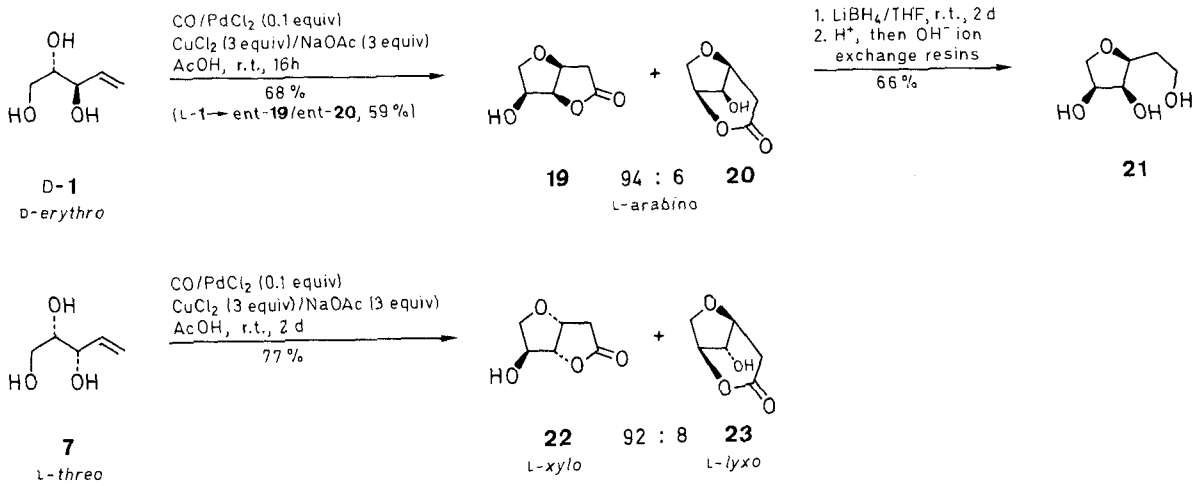
Scheme 2

Experimental Section). The dideoxy-hexenoses **14** and **17**, respectively, to the best of our knowledge have not been reported in the literature yet; we expect these to be highly interesting, versatile building blocks in other areas likewise.

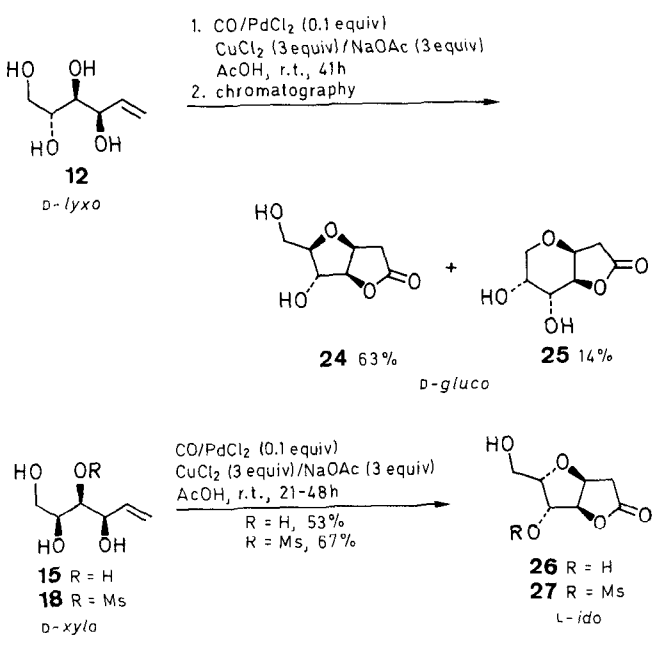
The oxycarbonylation of these enitol substrates was carried out with palladium(II) chloride (catalyst, 0.1 equiv.), copper(II) chloride (oxidant, 3 equiv.) and sodium acetate (buffer, 3 equiv.) in acetic acid under carbon monoxide at normal pressure and room temperature. This system, used in various Pd(II)-catalyzed reactions earlier,[47] had been shown to be advantageous for several *intra*molecular carbonylations,[19,27,28] while dichloromethane/methanol had been the preferred medium for 3-butenol cyclization/dicarbonylation.[20] The enitols used here (see Table 2) on such treatment all underwent slow conversion which could be monitored by colour change of the reaction suspension from green to yellow/ochre; the results are collected in Table 2 and Schemes **3**, **4**.

The major product in each case was identified by elemental analysis, IR, ^{1}H- and ^{13}C-NMR spectroscopy (Table 1, 3) as the respective 3,6-anhydro-1,4-aldonolactone, isolated in ca. 50–70% yield. With the pentenitols **1** and **7**, 6 to 11% of a second isomeric product, **20** and **23**, respectively, was formed; in the latter case this could be separated from the major product **22** chromatographically.

The mixture of the butyrolactone **19** and bridged valerolactone **20** on reduction with lithium borohydride furnished a single trisubstituted tetrahydrofuran **21** in 66% yield, suggesting that **19/20** were regioisomers. The coupling constants, $J_{2,3}$ = 5.0 and $J_{3,4}$ = 3.9 Hz,



Scheme 3



Scheme 4

indicate an all-*cis* configuration in **21**, and hence, the L-*arabino* configuration of both compounds **19/20**. The NMR data obtained for **19** on comparison with those of **22**, the butyrolactone formed from the L-*threo*-pentenitol **7**, bear the following evidence: the ^{1}H-NMR absorptions of the secondary CHO units at highest field (4.36 and 4.57 ppm, respectively), show a "'ddd" and "dd" pattern, respectively; from this and C,H-COSY results the conclusion is, that they originate from the non-acylated CHO-moiety with vicinal CH and CH_2 groups, that is they belong to 5-CHOH. With the latter (**22**), $J_{4,5}$ is *not* seen ($\approx$ 0 Hz); this is characteristic for a *trans* arrangement of H nuclei in such systems.[48] The ^{13}C-NMR chemical shifts obtained from **19/22** likewise evidence, by low-field displacements of the C-4, C-5, C-6 absorptions in **22**, the all-*cis* arrangement of substituents in the tetrahydrofuran part of **19**, as viewed against the *exo* arrangement of OH in **22** with *cis,trans*-configuration at the tetrahydrofuran ring. The ^{1}H- and ^{13}C-NMR data for **19** and ent-**22** that were published during the completion of our study[1,16] in almost all of the assignments corroborate this interpretation.

Table 2. Anhydro-2-deoxy-glyconolactones Prepared

Entry	Alkenitol (configuration)	Product(s) (configuration)	Ratio 1,4-/1,5-Glycono Lactone	Yield (%)	mp (°C) and/or bp (°C)/mbar	Molecular Formula[a, b]	IR[c] ν (cm^{-1})
1	D-**1** (D-*erythro*)	**19/20** (L-*arabino*)	94 : 6	68	57–58 140–150/0.01	$C_6H_8O_4$ (144.1)	3660–3040 (br s, OH), 2940 (m), 2860 (m), 1770 (s, CO), 1155 (s), 1070 (s), 1040 (s), 970 (m)
2	L-**1** (L-*erythro*)	ent-**19**/ent-**20** (D-*arabino*)	94 : 6	59	57–58 140–150/0.01	$C_6H_8O_4$ (144.1)	3660–3040 (br s, OH), 2940 (m), 2860 (m), 1770 (s, CO), 1155 (s), 1070 (s), 1040 (s), 970 (m)
3	**7** (L-*threo*)	**22/23** (L-*xylo*/L-*lyxo*)	89 : 11	77	79–81	$C_6H_8O_4$ (144.1)	3640–3040 (br s, OH), 2940 (m), 2860 (m), 1760 (s, CO), 1730 (s, CO), 1455 (m), 1180 (s), 1145 (s), 1065 (s), 1035 (s)
4	**12** (D-*lyxo*)	**24** (D-*gluco*)		63	49–51	$C_7H_{10}O_5$ (174.1)	3650–3060 (br s, OH), 2930 (m), 2870 (s), 2500 (m), 1775 (s, CO), 1445 (m), 1190 (s), 1000 (s), 880 (s)
		25 (D-*gluco*)		14	135–137	$C_7H_{10}O_5$ (174.1)	3420 (br m, OH), 2930 (m), 2530 (m), 1770 (s, CO), 1430 (m), 1005 (m), 870 (s)
5	**15** (D-*xylo*)	**26** (L-*ido*)		53	71–72	$C_7H_{10}O_5$ (174.1)	3620–3040 (br s, OH), 2935 (m), 2820 (m), 1771 (s, CO), 1390 (m), 1340 (m), 1185 (s), 1040 (s), 1020 (s)
6	**18** (D-*xylo*)	**27** (L-*ido*)		67	oil	$C_8H_{12}O_7S$ (255.2)	3630–3100 (br s, OH), 3002 (m), 2922 (m), 1775 (s, CO), 1345 (s), 1170 (s), 1045 (s), 950 (s)

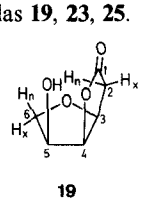
[a] Satisfactory microanalyses obtained: C ±0.32, H ±0.31.
[b] The enantiomerically pure compounds ent-**19** and **22** are reported in the reference 16; for ent-**19**: mp 77–78°C, **22**: mp 84–85°C (cf. Experimental Section).
[c] IR spectra recorded as a film, except for **25** ($CHCl_3$).

Table 3. ^{1}H-NMR Data of Compounds **19–27** Prepared[a, b, f]

Compound	Chemical Shifts δ								
	2-H_n	2-H_x	3-H	4-H	5-H	6-H_n	6-H_x	7-H_a, 7-H_b	Others
19	2.56	2.90	4.74	4.97	4.40	3.63	3.91	–	–
20	2.58	2.92	5.16–5.31	4.87	5.16–5.31	4.01	3.78	–	–
21	1.86	1.86	3.92	3.99	4.32	3.82	3.52–3.71	–	3.52–3.71 [1-H(CH_2OH)]
22	2.55	2.90	4.86–4.91	4.86–4.91	4.57	4.03	3.79	–	–
23	2.56	2.92	5.19–5.22	4.73–4.77	5.19–5.22	4.23	3.91	–	–
24	2.63	2.89	4.81–5.23	4.81–5.23	4.19–4.22	–	3.86	3.62, 3.74	–
25	2.42	2.87	4.41	4.47	4.18	–	3.81	3.58, 3.66	–
26	2.59	2.91	4.99	4.92	4.39	4.05	–	3.72, 3.80	–
27	2.61	2.92	5.20–5.28	5.20–5.28	4.83–5.12	4.23	–	3.74, 3.74	3.21 (SO_2CH_3)

Compound	Coupling Constants J (Hz)[c]										
	$J_{2n,2x}$	$J_{2n,3}$	$J_{2x,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6n}$	$J_{5,6x}$	$J_{6n,6x}$	$J_{6,7a}$	$J_{6,7b}$	$J_{7a,7b}$
19	18.7	1.6	6.7	5.0	5.0	6.9	6.0	9.0	–	–	–
20	18.4	1.4	9.3	1.9	1.9	4.2	2.1	10.1	–	–	–
21	–[d]	6.6	10.5	3.9	5.1	6.6	1.5	8.8	–	–	–
22	18.5	~0	5.7	–[d]	–[d]	4.0	2.0	10.1	–	–	–
23	18.6	~0	3.0	–[d]	–[d]	4.6	2.7	10.2	–	–	–
24	18.7	~0	5.0	–[d]	–[d]	–	5.7	–	5.8	3.7	11.9
25[e]	17.4	~0	4.5	3.0	2.7	–	2.7	–	6.0	3.1	10.7
26	18.7	~0	6.1	4.4	–[d]	3.3	–	–	6.4	4.8	19.2
27	18.9	~0	6.6	–[d]	–[d]	3.0	–	–	6.0	6.0	0

[a] Recorded at 200.1 (**19**, **20**, ent-**19**, ent-**20**) and 250.1 MHz (others) in CD_3OD.
[b] Values recorded for ent-**19** and ent-**20** in excellent agreement with those given for the enantiomeric compounds **19**, **20**.
[c] Long-range couplings observed in spectra from **19**/ent-**19** ($J_{2n,4} = 0.2$; $J_{4,6n} = 0.3$ Hz), **20** ($J_{2n,4} = 0.2$ Hz), **24** ($J_{2n,4} = 0.3$ Hz).
[d] Not identified due to overlapping signals.
[e] In DMSO-d_6 the OH absorptions show a doublet each, cf. experimental section.
[f] For numbering schemes and *endo*/*exo*-H designation cf. stereoformulas **19**, **23**, **25**.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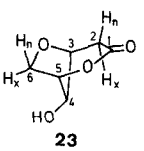
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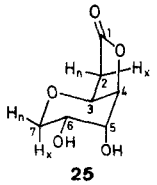

25

Table 4. ^{13}C-NMR Data of Compounds **19**–**27**[a,b,c]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7
19[d]	178.3	37.3	78.3	84.6	72.5	71.8	–
20	–[e]	36.6	78.5	74.2	82.7	70.6	–
21	60.3	33.7	80.5	73.5	73.3	72.4	–
22	177.9	36.7	78.6	90.1	75.4	72.6	–
23	–[e]	36.3	78.9	75.4	87.7	72.4	–
24	177.8	37.0	78.9	92.2	77.3	88.3	62.9
25	176.9	38.2	71.9	83.6	67.2	65.9	65.2
26	180.5	37.1	78.4	90.2	75.3	83.1	61.5
27[f]	177.4	36.6	82.5	87.5	78.6	81.4	60.6

[a] Recorded at 50.3 MHz (**19**, **20**, ent-**19**, ent-**20**) and at 62.9 MHz (others) in CD_3OD.
[b] Values recorded for ent-**19**, ent-**20** in excellent agreement with those given for the enantiomeric compounds **19**, **20**.
[c] Assignments for chemical shifts of **24**, **25**, **26**, **27** based on C,H-COSY measurements.
[d] The assignment of C-5/C-6 absorptions in reference 16 is reversed, according to the multiplicities registered here.
[e] Not detected.
[f] 38.3 (SO_2CH_3).

Table 5. ^{13}C-NMR Data of Enitols and Derivatives[a,b,c]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Others
D-**1**[32]	64.3	74.9	75.9	139.1	116.5	–	–
6	60.5	78.8	81.7	132.1	121.4	–	154.9 (CO)
7[d]	64.1	74.2	75.9	139.1	116.5	–	–
11	61.7	76.8[e]	80.5[e]	81.3[e]	136.0	116.8	25.2, 26.6 [C($\underline{C}H_3$)$_2$], 26.9 [C($\underline{C}H_3$)$_2$], 109.3, 109.6 [2 × $\underline{C}$(CH_3)$_2$]
12	63.8	71.5	71.8	74.1	140.7	114.4	–
13	104.6	75.7	80.8[e]	84.9[e]	131.2	119.9	26.1, 26.7 [C($\underline{C}H_3$)$_2$], 111.7 [$\underline{C}$(CH_3)$_2$]
15	64.5	73.0	75.0	74.9	139.3	116.9	–
16	106.2	81.4	85.3	84.9	132.3	120.8	26.7, 27.3 [($\underline{C}H_3$)$_2$], 38.6 ($SO_2\underline{C}H_3$), 113.7 [$\underline{C}$(CH_3)$_2$]
18	63.1	70.9	85.9	71.9	137.1	117.0	38.2 ($SO_2\underline{C}H_3$)

[a] Recorded at 50.3 MHz (D-**1**, L-**1** in CD_3OD, **13** in $CDCl_3$), at 100.6 MHz (**11** in $CDCl_3$) and at 62.9 MHz (**6**, **7**, **15**, **16**, **18** in CD_3OD, **12** in DMSO-d_6).
[b] Values recorded for L-**1** in excellent agreement with those given for the enantiomeric compound D-**1**.[32]
[c] Assignments for chemical shifts of **15** based on C,H-COSY measurement.
[d] The *erythro*-pentenitol D-**1**[30,32] and the *threo* isomer **7** are hardly distinguishable by ^{13}C-NMR spectra when recorded separately. The following values were obtained from a mixture (57 mg of D-**1**/17 mg of **7** in 0.5 mL CD_3OD); values of **7** given in parentheses: δ = 64.29 (64.07), 74.81 (74.28), 75.92 (75.92), 116.51 (116.47), 139.18 (139.03).
[e] Probable assignments, may eventually be reversed.

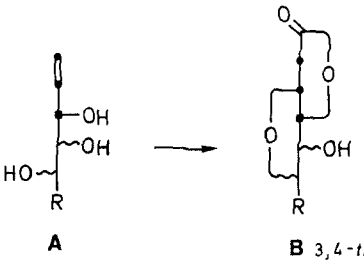
The structure and configuration of the minor products **20** and **23** from the oxycarbonylation of *erythro*- and *threo*-pentenitols **1** and **7**, respectively, were deduced from NMR data in a similar way. In the case of the (94:6)-mixture of **19/20**, the *structure* of the secondary product **20** became obvious from the chemical shift changes for C-4 and C-5 – 90.1/75.4 for C-4/C-5 of **19** switching to 75.4/87.4 in **20**, reflecting the transition from the 5-membered lactone with 4-*O*-acylation to the 6-ring lactone in **20**. Similar arguments were applied to assign structure and configuration of **23**.

The oxycarbonylation of the hexenitols **12**, **15**, and **18** gave the bicyclic ([3.3.0]) butyrolactones **24**, **26**, and **27** respectively; see Table 2. From the close agreement of the spectroscopic data obtained for **24** with those of the L-*xylo*-hexenolactone **22**, the configuration of the newly generated stereocentres (C-3, C-4), and thence the D-*gluco*-arrangement in **24** is derived. The products **26** and **27**, resulting from the D-*xylo*-hexenitols **15** and **18**, show ^{1}H- and ^{13}C-NMR data as expected for the change of C-6 configuration from **24** (D-*gluco*) to **26/27** (L-*ido*). Independent support for these assignments comes from a recent paper on novel bioactive styryl-lactones, notably goniofufurone, a 7-phenyl-substituted 3,6-anhydro-2-deoxy-heptonolactone of *glycero-ido*-configuration (absolute configuration not known);[49] the ^{1}H coupling parameters and ^{13}C chemical shifts given there nicely parallel the respective numbers of the L-*ido* compound **26**.

The oxycarbonylation of the 4-*lyxo*-hexenitol **12** besides **24** furnished a second isomer, **25**, which was obtained pure by chromatographic separation (14% yield). The NMR data, in particular the absorptions of 3-H, 4-H, 5-H, and of C-3 to C-6, showed substantial differences to those recorded for the other two types of anhydrolactones dealt with so far. From C,H-COSY experiments all proton and carbon resonances were assigned, expect for 4-H/5-H and C-4/C-5. The ^{1}H-NMR spectrum taken in DMSO-d_6 showed two doublets for the OH signals pointing to the presence of two CHOH fragments; an IR absorption at 1770 cm^{-1} indicated a 1,4-lactone part. With these pieces of information, ^{13}C-NMR data of substructures – the bicyclic lactones **19/20** and the reduced monocycle **21**, pento-pyranoses and their methyl glycosides,[50] furanoses and anhydroalditols[50] – were screened. Surprisingly (*vide infra*), the unambiguous conclusion was that **25** is 3,7-anhydro-2-deoxy-(D)-*gluco*-1,4-heptonolactone, with the $^4C_1$ solution conformation. With branched substrates, *erythro*/*threo*-3-hydroxymethyl-4-pentene-1,4-diols, oxycarbonylation had only resulted in tetrahydrofuran/γ-lactone formation as shown in Table 1; none of the tetrahydrofuran products from the competing cyclization mode had been detectable there.[19] On the other hand, such products were the only ones formed from 1,4-diols with an intermittent *o*-phenylene moiety that does not permit other types of bicyclization (see Table 1).[23]

The mechanistic course of the fascinating, oxycarbonylating bicyclization of unsaturated polyols and the like has not been established in detail yet.[19,24,27] This concerns the role and directing power of variously placed OH groups, the reversibility of the several steps prior to CO insertion into the Pd–C bond, and the sequence of steps (proven or likely) involved – Pd(II)/C=C coordination, sparking the nucleophile's attack to form the first ring with a terminal σ-Pd-C species, CO → Pd coordination plus Pd–C insertion as the C-elongation step, lactonization to the bicyclic product with extrusion of PdX_mL_n, representing or collapsing to Pd(0), which is reverted to

Pd(II) by the $CuCl_2$ oxidant, to re-enter the catalytic cycle.[19-24,27] Concerning the aspect "utility for organic synthesis", the above first applications of this reaction to optically active and carbohydrate-derived alkenitols demonstrate that bicyclization to afford anhydroaldonolactones of the [3.3.0]-type is the dominating process, and thus should be taken as a new, viable alternative for homologation of alkenitols, to arrive at C-glycosidic structures in a predictable manner. The principle of the above transformations may be summarized by formulas **A** and **B** showing that the configuration at the allylic centre induces the generation of the new stereocentre in a *threo*-selective manner:



A **B** 3,4-*threo*

Thus, starting from D-glucose (or L-idose), via the D-*xylo*-hexenitol, the anhydro-1,4-heptonolactone **26** of L-*ido* configuration is produced; starting from D-allose, the L-*altro* homologue is expected, D-galactose would convert to L-*galacto* etc.

That there is at least two additional, although minor bicyclization pathways, not due to product equilibration, shows *some* effect of the substrate configuration that should be elucidated further. It seems highly promising to introduce further (C_6 and higher) alkenitols to this reaction and to provide partially protected substrates for this, in order to arrive at product structures disfavoured from the free polyols, in a regiocontrolled and stereoselective manner.

A conclusion to be drawn from this study is that the Pd(II)-catalyzed carbonylation of complex C,C-unsaturated substrates, loaded with several *a priori* competing nucleophilic functional groups, may turn out highly selective and be useful in organic synthesis. Unsaturated polyols are at hand in abundance, that is great variety concerning structures, stereoisomers and partially protected congeners, from iso-skeletal precursors as employed here or, for example, Takano's recent extension of the asymmetric Sharpless epoxidation to divinylglycols.[51] Moreover, access to suitable substrates by $(C_n + C_1)$-, $(C_n + C_2)$-, and $(C_n + C_3)$-strategies, e.g. by Wittig methylenation, vinyl or allyl metal-effected aldehyde C-elongation, is well established[2-4,8,9] and may be drawn upon at anyone's discretion.

Solvents and reagents were purified and dried according to standard procedures. Ion exchange resins (strongly acidic: Lewatit SPC 118, $H^{\oplus}$ form; medium basicity: Lewatit MP 64, $^{\ominus}OH$ form; strongly basic: Lewatit M 500 KR, $^{\ominus}OH$ form) were obtained from Bayer AG, Leverkusen; $CuCl_2$ (Aldrich), $PdCl_2$ (Janssen), monoacetone glucose (Janssen) and D-ribonolactone (Fluka) were purchased. 1,4-Pentadien-3-ol was prepared as described[52] or purchased from Aldrich. Reactions in acetone at 100°C were carried out in 100 to 250 mL steel autoclaves (Fa. C. Roth, Karlsruhe).

TLC analyses were carried out with Si60 F_{254}-coated aluminum sheets (E. Merck) using EtOAc/petroleum ether (bp 30–75°C) mixtures; detection by UV at 254 nm, phosphomolybdic acid (10% in EtOH) or sulfuric acid (40% in H_2O). Silica 32–63 μm (Woelm) was used for flash chromatography, eluents as above. Melting points were determined on a Tottoli apparatus or a heat bar (system Kofler) and are uncorrected. Bp's refer to bath temperatures of Kugelrohr distillations. The optical rotations were measured on a Perkin-Elmer 241 MC polarimeter using the Drude method to calculate $[\alpha]_D$ from the values found for 546 and 579 nm. IR spectra were recorded on a Perkin-Elmer 4120 spectrometer. NMR spectra were obtained from Varian EM 390, Bruker AC 200, 250 and WM 400 spectrometers (^1H: 90, 200.1, 250.1, 400.1 MHz; ^{13}C: 50.3, 62.9, 100.6 MHz) with TMS as internal standard (δ = 0.00 ppm); evaluation of ^1H-NMR spectra according to 1st order interpretation; multiplicity of ^{13}C-NMR signals from broad band-decoupled or DEPT spectra. *endo*- and *exo*-Situated H are designated H_n, H_x.

Preparation of Enitols D-1, L-1, 7

(2*S*,3*R*)-4-Pentene-1,2,3-triol (D-1) was prepared from D-ribonolactone in 5 steps with 50% overall yield, bp 120–130°C/0.2 mbar, $[\alpha]_D^{22}$ +27.4° (*c* = 1.16, MeOH), as reported earlier[30,31] {Lit.[30,31] 50%, bp 120–130°C/0.2 mbar, $[\alpha]_D^{18}$ +27.7° (*c* = 2.06, MeOH)}.

(2*R*,3*S*)-4-Pentene-1,2,3-triol (L-1) was obtained from 1,4-pentadien-3-ol by asymmetric Sharpless epoxidation followed by acidic hydrolysis,[30,32] ca. 40% overall yield, bp 120–140°C/0.2 mbar, $[\alpha]_D^{22}$ −22.9° (*c* ≈ 1.08, MeOH) {Lit.[30,32] 37–61%, bp 140–160°C/0.1 mbar, $[\alpha]_D^{18}$ −25.8° (*c* ≈ 1.39, MeOH)}.

(2*S*,3*S*)-Pentene-1,2,3-triol (7):

(2R,3S)-3-(Benzylaminocarbonyloxy)-1,2-epoxy-4-pentene **(5)**:

Prepared as described for the enantiomer,[35] epoxide **2**[30,32] [1.06 g of a mixture with 6% *t*-BuOOH/*t*-BuOH, $[\alpha]_D^{23}$ +59.1° (*c* ≈ 1.34, $CHCl_3$), corresponding to 1.00 g, 10.0 mmol of **2**] in CH_2Cl_2 (anhydrous, 60 mL), to which at 0°C benzyl isocyanate (1.60 g, 12.0 mmol) was added; hydrolysis with sat. $NaHCO_3$ solution (10 mL) after 4 d at r.t.; extraction with CH_2Cl_2 (3 × 15 mL), flash-chromatographic purification (silica gel, 56 g); column 27 cm × 2 cm; eluent petroleum ether/EtOAc 1:1). Yield of epoxy urethane **5**: 2.02 g (87%), yellow, waxy material; $[\alpha]_D^{23}$ −30.8° (*c* ≈ 0.600, $CHCl_3$) {Lit.[35] 67%, $[\alpha]_D^{22}$ +24.6° (*c* ≈ 0.223, $CHCl_3$) found for the enantiomer}; IR, ^1H- and ^{13}C-NMR data in accord with those recorded for ent-**5**.[35]

$C_{13}H_{15}NO_3$	calc.	C 66.94	H 6.48	N 6.00
(233.3)	found	66.56	6.61	5.98

(2S,3S)-2,3-Carbonyldioxy-4-penten-1-ol **(6)**:

For cyclization,[39] to the epoxy-urethane **5** (1.58 g, 6.80 mmol) in Et_2O (75 mL) is added dropwise at 0°C $Et_2O \cdot BF_3$ (2.76 g, 19.5 mmol) within 20 min, causing a colourless precipitate. With continued stirring at 0°C for 2 h, 2N H_2SO_4 (50 mL) is added to form a second phase; the mixture is stirred at r.t. for 17 h. The organic layer is separated, the aqueous layer is extracted with Et_2O (5 × 20 mL), the organic solutes are combined and dried (Na_2SO_4). After concentration at 30–40°C/20 mbar the remainder is purified by flash chromatography (cf. above; 28 g of silica, column 22 cm × 1 cm, petroleum ether/EtOAc 6:4); yield of carbonate **6** 650 mg (66%), colourless oil; $[\alpha]_D^{25}$ −70.5° (*c* = 0.605, $CHCl_3$) {found for ent-**6**:[35] $[\alpha]_D^{22}$ +69.0° (*c* = 0.15, $CHCl_3$)}.

$C_6H_8O_4$	calc.	C 50.00	H 5.60
(144.1)	found	49.82	5.73

IR ($CHCl_3$): ν = 3550, 3380 (br s), 3060 (m), 1795 (vs), 1590 (m), 1360, 1160, 1020 cm^{-1}.

^1H-NMR ($CDCl_3$): δ = 3.70 (dd, 1 H, 1-H_a), 3.80 (br s, 1 H, OH), 3.98 (dd, 1 H, 1-H_b), 4.40 ("dt", 1 H, 2-H), 5.05 (tt, 1 H, 3-H), 5.42 (dt, 1 H, 5-H_E), 5.50 (dt, 1 H, 5-H_Z), 5.91 (ddd, 1 H, 4-H). Coupling constants: $J_{1a,1b}$ = 13.1, $J_{1a,2}$ = 3.3, $J_{1b,2}$ = 2.9, $J_{2,3} = J_{3,4}$ ≈ 7.0, $J_{3,5E} = J_{3,5Z} = J_{5E,5Z}$ = 0.9, $J_{4,5E}$ = 10.3, $J_{4,5Z}$ ≈ 17.3 Hz.

(2S,3S)-Pentene-1,2,3-triol (**7**):

For acidic hydrolysis[36] the carbonate **6** (230 mg, 1.60 mmol) is heated to reflux for 16 h in MeOH (4.5 mL) with 6 N HCl (0.8 mL). After removal of volatiles at ca. 20 mbar H_2O (5 mL) is added and the mixture partitioned with CH_2Cl_2 (5 mL), to separate from lipophilic impurities. The aqueous phase is concentrated in vacuo to leave the triol **7** as a yellow oil, analytically pure; yield 182 mg (96%); $[\alpha]_D^{25}$ −46.2° (*c* = 0.175, MeOH) {Lit.[32] $[\alpha]_D^{20}$ ca. +48° [estimate from a 62:38 mixture of L-**1**/ent-**7** derived from D-glyceraldehyde acetonide]}.

$C_5H_{10}O_3$ (118.2) calc. C 50.83 H 8.55 found 51.06 8.86

IR (film): *ν* = 3660–3020 (br s), 2920 (m), 2880 (m), 1720 (w), 1675 (w), 1660 (vw), 1435 (m), 1255 (m), 1080 (s), 1035 (s), 990 (m), 935 (m), 845 (m) cm^{-1}.

^{1}H-NMR (CD_3OD): *δ* = 3.46–3.56 (m, 2H, 1-H), 3.61–3.69 (m, 1H, 2-H), 4.08 (tt, 1H, 3-H), 5.16 (dt, 1H, 5-H_E), 5.29 (dt, 1H, 5-H_Z), 5.92 (ddd, 1H, 4-H). Coupling constants: $J_{2,3} = J_{3,4} = 6.1$, $J_{3,5E} = J_{3,5Z} = 1.6$, $J_{4,5E} = 10.4$, $J_{4,5Z} = 17.1$ Hz.

(2R,3S,4R)-5-Hexene-1,2,3,4-tetrol (D-*lyxo*-5-Hexenitol; 12):

*1,2:3,4:5,6-Tri-O-isopropylidene-*D*-mannitol* [D-mannitol tris(acetonide); **8**] was prepared from D-mannitol (25.0 g, 0.137 mmol) with acetone/sulphuric acid as described;[53] yield 17.4 g (41%), mp 66–67°C, $[\alpha]_D^{24}$ +16.5° (*c* = 1.395, MeOH) {Lit.[53] 75% mp 69–70°C, $[\alpha]_D$ not given; the literature yield was not parallelled in several runs by different experimenters}.

*1,2:3,4-Di-O-isopropylidene-*D*-mannitol* (**9**) was obtained from **8** (17.62 g, 58.3 mmol) in EtOH/H_2O with conc. HCl (1.2 mL); the crude product consisting of educt **8** and **9** was separated by flash chromatography (silica 40 g, column 15 cm × 3 cm; eluent petrol ether/EtOAc 7:3, then pure EtOAc) to afford **8** (11.27 g, 58%) and (bis)acetonide **9** (4.09 g, 27%; corrected yield 64%); colourless crystals, mp 35–37°C, $[\alpha]_D^{24}$ +26.3° (*c* = 0.625, MeOH) {Lit.[53] 34.5%, mp 37°C, $[\alpha]_D$ not stated}.

IR (film): *ν* = 3460 (br s, OH), 3000 (s), 2950 (m), 1385, 1375 (CMe_3), 1240, 1215, 1070 cm^{-1} (all s).

^{1}H-NMR ($CDCl_3$): *δ* = 1.40 (s, 9H, 3 × CH_3), 1.45 (s, 3H, CH_3), 2.55 (br s, 1H, OH), 3.60–4.33 (m, 9H, 4 × CH, 2 × CH_2, OH).

*1,2:3,4-Di-O-isopropylidene-5,6-di-O-mesyl-*D*-mannitol* (**10**):

At 0°C, MsCl (0.38 mL, 566 mg, 4.90 mmol) in pyridine (1.5 mL) is added dropwise to a pyridine (1.5 mL) solution of **9** (481 mg, 1.80 mmol). After 15 h at 0°C the mixture is poured on ice/water (20 mL) to form a yellow precipitate, which is filtered and crystallized from MeOH; yield 676 mg (90%) of **10**, colourless crystals, mp 117.5–118°C, $[\alpha]_D^{23}$ +24.7° (*c* = 2.18, $CHCl_3$) {Lit.[40]: 88%; mp 118–120°C; $[\alpha]_D^{20}$ +25.1° (*c* = 2.0, $CHCl_3$)}.

(2R,3S,4R)-1,2:3,4-Bis(isopropylidenedioxy)-5-hexene [D-*lyxo*-5-*Hexenitol Bis(acetonide)*; **11**]:

Varying the procedure given by Bladon and Owen,[40] the dimesylate **10** (5.00 g, 10.4 mmol) and NaI (15.0 g, 100 mmol) are dissolved in acetone (100 mL) and heated to 100°C for 6.5 h in a 250 mL-autoclave (C. Roth GmbH, Karlsruhe). The mixture is concentrated in vacuo: the dark-red residue is dissolved in $CHCl_3$ (10 mL) and treated with $Na_2S_2O_3$ solution (10% in H_2O) until completely decoloured. After separation the aqueous layer is extracted with $CHCl_3$ (5 × 15 mL), the organic solutes are combined, once more washed with sat. $Na_2S_2O_3$ solution (25 mL), dried (Na_2SO_4), and concentrated (rotary evaporator). The resulting oil is distilled (Kugelrohr; 70–80°C/1 mbar) to give an orange oil (2.385 g, 100%) which, dissolved in $CHCl_3$ (5 mL), is again treated with $Na_2S_2O_3$ solution (2 × 10 mL) and dried (Na_2SO_4). Removal of the solvent at 0.01 mbar gives **11** as a colorless, analytically pure oil; yield 2.19 g (92%), $[\alpha]_D^{21}$ −5.3° (*c* = 2.98, $CHCl_3$) {Lit.[40] 66%, $[\alpha]_D^{21}$ −5.5° (*c* = 2.4, $CHCl_3$)}.

IR (film): *ν* = 3000 (s), 2950 (s), 2890 (m), 1385, 1375 (CMe_3), 1250, 1215, 1070 cm^{-1} (all s).

^{1}H-NMR ($CDCl_3$): *δ* = 1.30, 1.40 (2 s, 2 × 3H, $2CH_3$), 1.41 (s, 6H, $2CH_3$), 3.75 and 3.95 (AB of ABC, 2H, 1-H), 4.11 (mc, 2-H_C, 3-H), 4.36 ("tt", 1H, 4-H), 5.21 and 5.41 (A'B' of A'B'X', 2H, 6-H_E and 6-H_Z), 5.91 (dX', 1H, 5-H). Coupling constants: $J_{AB} = J_{AC} = 7.5$, $J_{BC} = 4.5$, $J_{3,4} = J_{4,5} = 6.25$, $J_{4,6} = 1.25$, $J_{5,6E} = 10.6$, $J_{5,6Z} = 16.75$, $J_{6E,6Z} = 1.25$ Hz.

(2R,3S,4R)-5-Hexene-1,2,3,4-tetrol (D-*lyxo*-5-Hexenitol; **12**):

An emulsion of the bis(acetonide) **11** (1.76 g, 7.71 mmol) in 2N AcOH (15 mL) is heated under reflux for 2 h (TLC control; eluent petroleum ether/EtOAc 8:2). After concentration in vacuo the remainder is dried (desiccator; KOH) to give analytically pure **12** as a colourless powder; yield 1.11 g (97%), mp 147–149°C. From another sample, analytically pure likewise (96% yield): mp 145–146°C, $[\alpha]_D^{22}$ +32.1° (*c* = 1.005, MeOH) {Lit.[40] mp 147–148°C, $[\alpha]_D^{20}$ +30.0° (*c* = 1.0, H_2O); Lit.[45] mp 148.5–149°C, $[\alpha]_D^{20}$ +33.4° (*c* = 1.0, H_2O).

IR (KBr): *ν* = 3280 (br s, OH), 3190, 1645, 1285, 1075, 1030, 920 cm^{-1}.

^{1}H-NMR (DMSO-d_6): *δ* = 3.15–3.27 (m, 1H, 3-H), 3.34–3.51 (m, 2H, 1-H), 3.53–3.61 (m, 1H, 2-H), 4.15–4.20 (m, 1H, 4-H), 4.34 (t, 1H, 1-OH), 4.35, 4.52, 4.54 (3 d, 3H, 3 × OH), 5.07 (dt, 1H, 6-H_E), 5.19 (dt, 1H, 6-H_Z), 5.92 (ddd, 1H, 5-H). Coupling constants: $J_{4,6Z} = J_{6E,6Z} = 1.6$, $J_{1,OH} = 5.5$, $J_{2,OH}$, $J_{3,OH}$ and $J_{4,OH}$: 6.2, 6.9 and 7.6, $J_{5,6E} = 10.6$, $J_{5,6Z} = 17.0$ Hz.

(2S,3S,4R)-5-Hexene-1,2,3,4-tetrol (D-*xylo*-5-hexenitol; 15):

D-*xylo*-Hexenitol **15** was prepared earlier from D-sorbitol via the bis(ethylidene)-acetal and the ensuing 5,6-bis(tosylate) in 4 steps and 5% overall yield.[40] The route presented here affords 16% of **15**, after 4 steps from monoacetone glucose.

*1,2-O-Isopropylidene-5,6-di-O-tosyl-α-*D*-glucofuranose:* Prepared from monoacetone glucose (10 g, 45 mmol), according to Lit.,[41] yield 8.37 g (35%), colourless crystals, mp 160–161°C {Lit. 40%,[41] mp 160,[54] 161–162°C,[41] $[\alpha]_D$ −6.37° (*c* = 1.27, $CHCl_3$),[54] $[\alpha]_D$ −6.85° (*c* = 2.7, $CHCl_3$)[41]}.

*1,2-O-Isopropylidene-α-*D*-xylo-5-hexenofuranose* (**13**):

The bis(tosylate) (6.73 g, 12.0 mmol) with NaI (11.2 g, 75.0 mmol) in acetone (100 mL) is heated in an autoclave to 100°C for 14 h, as described.[41] Yield 1.87 g (84%), colourless crystals, mp 58–59°C, $[\alpha]_D^{25}$ −52.9° (*c* = 2.100, $CHCl_3$) {Lit.:[41] 85%, mp 61–65°C (after sublimation), $[\alpha]_D^{25}$ −51.5° (*c* = 1.1, $CHCl_3$)}. After completion of these studies, we realized and verified that that access to **13** is more conveniently gained by LiAlH reduction of **16**, cf. Lit.[3] (Vasella).

^{1}H-NMR ($CDCl_3$): *δ* = 1.33, 1.51 [2 s, 6H, $C(CH_3)_2$], 2.04 (d, 1H, OH), 4.10 (dd, 1H, 3-H), 4.58 (d, 1H, 2-H), 4.73 (m, 1H, 4-H), 5.42 (dt, 1H, 6-H_Z), 5.54 (dt, 1H, 6-H_E), 5.90 (ddd, 1H, 5-H), 5.95 (d, 1H, 1-H). Coupling constants: $J_{1,2} = 3.8$, $J_{2,3} < 0.5$ (not resolved), $J_{3,OH} = 3.8$, $J_{3,4} = 2.3$, $J_{4,5} = J_{5,6E} = 10.6$, $J_{5,6Z} = 17.4$, $J_{4,6E} = J_{4,6Z} = J_{6Z,6Z} = 1.6$ Hz.

*α/β-*D*-xylo-5-Hexenofuranose* (**14**):

The hexenofuranose acetonide **13** (1.867 g, 10.0 mmol), dissolved in aq AcOH (1:1, 25 mL), is heated to 90° for 18 h (TLC-monitoring). Removal of solvents in vacuo (20 mbar) leaves a yellow oil which is purified by chromatography on silica gel 820 g; column 1.8 cm × 10 cm, eluent EtOAc). The furanose **14** is obtained as a yellow, but analytically pure oil; yield 1.274 g (87%), $[\alpha]_D^{22}$ −2.9° (*c* = 0.850, MeOH).

$C_6H_{10}O_4$ (146.1) calc. C 49.31 H 6.90 found 49.52 7.27

IR (film): *ν* = 3350 (s, OH), 2922 (m), 2500 (w), 1635 (w), 1420 (m), 1018 (s), 925 (s) cm^{-1}.

^{1}H-NMR (CD_3OD): *δ* = 3.41–3.77 and 3.94–3.99 (2 m, 1H each, 2-H, 3-H), 4.05–4.36 (m, 1H, 4-H), 4.55–4.62 (m, 1H, 1-H), 5.16–5.41 (m, 2H, 6-H), 5.82–6.09 (m, 1H, 5-H).

^{13}C-NMR (CD_3OD), mixture of 4 isomers (?): *δ* = 74.06, 74.31, 74.37, 74.46, 75.49, 75.60, 77.97, 78.82, 81.73, 82.23, 84.84 (all d; C-2, C-3, C-4), 97.76, 99.21, 99.47, 104.17 (all d, relative peak intensities

44:8:38:10; C-1), 117.52, 117.60, 118.46, 118.51 (all t, the latter two stem from the major products; C-6), 135.64, 136.06, 139.03 (all d, C-5).

(2S,3S,4R)-5-Hexene-1,2,3,4-tetrol **(15)**:

The aldofuranose **14** (908 mg, 6.21 mmol), dissolved in H_2O (10 mL), at r.t. is slowly (ca. 20 min) added to a solution of $NaBH_4$ (235 mg, 6.21 mmol) in H_2O (10 mL).[44] The mixture is stirred until gas evolution cases (ca. 90 min), with the pH of the solution changing to 9–10. H_2O (50 mL) and conc. H_2SO_4 (several drops) are added to attain pH 6–7. The resulting solution is passed through columns (8 cm × 18 cm) loaded with ion exchange resins (Lewatit SPC 118, $H^{\oplus}$-form, strongly acidic, 12 g; then Lewatit MP 64, $^{\ominus}$OH-form, medium basicity, 12 g).[44] The eluate is concentrated in vacuo (20 mbar) and leaves a spectroscopically and analytically pure, colourless oil **15**; yield 592 mg (64%); $[\alpha]_D^{22}$ + 16.2° (*c* = 0.550, MeOH) {Lit.[40] $[\alpha]_D^{19}$ + 19.8° (*c* = 3.8, H_2O}.

IR (film): *v* = 3340 (s, OH), 2920, 2880, 2480 (s), 2068, 1632 (w), 1420, 1012, 970 (s) cm^{-1}.

^{1}H-NMR (CD_3OD; C,H-COSY): δ = 3.51 (dd, 1 H, 3-H), 3.59–3.71 (m, 2 H, 1-H), 3.74 (mc, 1 H, 2-H), 4.24 ("ddt", 1 H, 4-H), 5.23 (dt, 1 H, 6-H_E), 5.38 (dt, 1 H, 6-H_Z), 5.98 (ddd, 1 H, 5-H). Coupling constants: $J_{2,3}$ = 2.6, $J_{3,4}$ = 6.1, $J_{4,5}$ = 6.3, $J_{4,6E}$ = $J_{4,6Z}$ = 1.3, $J_{5,6E}$ = 10.4, $J_{5,6Z}$ = 17.2, $J_{6E,6Z}$ = 1.4; $J_{1,2}$ not interpretable from 1st order analysis.

(2*S*,3*S*,4*R*)-3-Mesyloxy-5-hexene-1,2,4-triol (3-*O*-Mesyl-D-xylo-5-hexenitol; 18):

1,2-O-Isopropylidene-3,5,6-tri-O-mesyl-α-D-gluco-furanose: Prepared according to lit.[55] from monoacetone glucose (22.6 g, 10.3 mmol); yield 18.8 g (83%), mp 158–159°C, $[\alpha]_D^{25}$ −31.8° (*c* = 1.030, $CHCl_3$) {Lit.[55] 90.5% after one crystallization from pentane/$CHCl_3$, mp 162–163°C, $[\alpha]_D^{22}$ −20.4° (*c* = 1.81, Py)}.

1,2-O-Isopropylidene-3-O-mesyl-α-xylo-5-hexenofuranose **(16)**:

From the above tris(mesylate) (11.4 g, 25.1 mmol) with NaI (29.5 g, 19.6 mmol) in acetone (100 mL) at reflux for 15 h, as described.[42] Yield: 4.8 g (73%), after crystallization from EtOH/H_2O (4:1); mp 78–81°C, $[\alpha]_D^{25}$ −42.2° (*c* = 1.24, $CHCl_3$); Lit.[42]: 87%, mp 78–81°C.

^{1}H-NMR ($CDCl_3$): δ = 1.34, 1.53 (2 s, 2 × 3 H, $2CH_3$), 3.04 (s, 3 H, SO_2CH_3), 4.78 (m, 1 H, 4-H), 4.81 (d, 1 H, 2-H), 4.97 (d, 1 H, 3-H), 5.40 (dt, 1 H, 6-H_E), 5.51 (dt, 1 H, 6-H_Z), 5.88 (ddd, 1 H, 5-H), 5.99 (d, 1 H, 1-H). Coupling constants: $J_{1,2}$ = 3.8, $J_{2,3}$ < 0.5 (not resolved), $J_{3,4}$ = 2.9, $J_{4,5}$ = 6.4, $J_{4,6E}$ = $J_{4,6Z}$ = $J_{6E,6Z}$ = 1.2, $J_{5,6E}$ = 10.5, $J_{5,6Z}$ = 17.3 Hz.

3-O-Mesyl-α/β-D-xylo-5-hexenofuranose **(17)**:

The mesyl-furanose **16** (4.00 g, 15.1 mmol) is dissolved in AcOH/H_2O (1:1, 50 mL) and heated to 90°C for 10 h (TLC control). After cooling, the mixture is stirred with ion exchange resin (1 g, $^{-}$OH-form, Lewatit M 500 KR/OM, strongly basic, Bayer AG) for 1 h and then concentrated in vacuo (20 mbar). The resulting yellow oil is submitted to chromatography (silica, 30 g, column 10 cm × 3 cm, eluent petroleum ether/EtOAc 1:1). Yield of **17** as a yellow oil: 2.862 g (85%), R_f 0.44 (with EtOAc), $[\alpha]_D^{20}$ + 23.2° (*c* = 1.190, MeOH).

$C_7H_{12}O_6S$ calc. C 37.50 H 5.39
(224.2) found 37.97 5.64

IR (film): *v* = 3450 (s, OH), 2960, 2930, 1709 (m), 1340, 1170, 930 (all s) cm^{-1}.

^{1}H-NMR (CD_3OD); mixture of isomers: δ = 3.08, 3.10, 3.11 (3 s, 3 H, SO_2CH_3), 4.18–4.28 (m, 1 H, 2-H), 4.64–4.75 (m, 1 H, 1-H), 4.79–4.87 (m, 1 H, 4-H), 4.91–5.02 (m, 1 H, 3-H), 5.23–5.47 (m, 2 H, 6-H), 5.79–6.01 (m, 1 H, 5-H).

^{13}C-NMR (CD_3OD); mixture of isomers: δ = 2 × 37.54, 38.35, 38.39 (SO_2CH_3), 72.33, 72.42, 75.99, 77.77, 77.95, 79.31, 80.22, 81.09, 81.88, 84.66, 85.50, 85.90 (C-2, C-3, C-4), 95.77, 97.35, 97.45, 102.89 (all d, relative peak intensities 43:35:12:10; C-1), 117.40, 117.51, 118.51, 118.68 (C-6), 133.19, 133.56, 136.88, 136.97 (C-5).

(2S,3S,4R)-3-Mesyloxy-5-hexene-1,2,4-triol **(18)**:

The $NaBH_4$ reduction and work-up are carried out as described for the unprotected hexenitol **15** (*vide supra*); from **17** (1.30 g, 5.79 mmol) with $NaBH_4$ (227 mg, 5.79 mmol) the crude product (1.11 g) is obtained as a colourless oil which is purified by passage through a short silica-filled column (30 g of silica, column 3 cm × 10 cm; eluent EtOAc). Yield 989 mg (73%), R_f 0.23 (EtOAc), $[\alpha]_D^{20}$ + 17.2° (*c* = 1.060, MeOH).

$C_7H_{14}O_6S$ calc. C 37.16 H 6.24
(226.2) found 37.22 6.50

IR (film): *v* = 3350 (s, OH), 2930, 1635, 1410, 1325, 1165, 1118, 925, 832 cm^{-1}.

^{1}H-NMR (CD_3OD): δ = 3.21 (s, 3 H, SO_2CH_3), 3.68 ("ddd", 2 H, 1-H), 3.89 ("ddd", 1 H, 2-H), 4.48 (ddt, 1 H, 4-H), 4.62 (dd, 1 H, 3-H), 5.30 (dt, 1 H, 6-H_E), 5.46 (dt, 6-H_Z), 6.01 (ddd, 1 H, 5-H). Coupling constants: $J_{1A,1B}$ = 11.3, $J_{1A,2}$ = 5.1, $J_{1B,2}$ = 6.2, $J_{2,3}$ = 4.0, $J_{3,4}$ = $J_{4,5}$ = 6.1, $J_{4,6E}$ = $J_{4,6Z}$ = 1.2–1.5, $J_{5,6E}$ = 10.45, $J_{5,6Z}$ = 17.2, $J_{6E,6Z}$ = 1.45 Hz.

Alkoxycarbonylation; 3,6-Anhydro-1,4-aldonolactones:

3,6-Anhydro-2-deoxy-L-*arabino*-1,4-hexonolactone {(1*R*,5*S*,8*S*)-8-Hydroxy-2,6-dioxabicyclo[3.3.0]octan-3-one, 19} and 3,6-Anhydro-2-deoxy-L-*arabino*-1,5-hexonolactone {(1*S*,5*S*,8*R*)-8-Hydroxy-2,6-dioxabicyclo[3.2.1]octan-3-one, 20}; Typical Procedure:

A 50 mL-flask, purged with CO and connected to a balloon filled with CO, is charged with $PdCl_2$ (25 mg, 0.138 mmol), $CuCl_2$ (anhydrous; 557 mg, 4.14 mmol), NaOAc (anhydrous; 340 mg, 4.14 mmol), (2*S*,3*R*)-4-pentene-1,2,3-triol (D-**1**, 163 mg, 1.38 mmol), and AcOH (10 mL). The deep green mixture is stirred at r.t. for 16 h (until coloured yellow to ochre), then filtered through a short tube filled with cellulose. AcOH is removed on a rotavapor (20 mbar), the residue is distilled (Kugelrohr, bath temp. 140–150°C/0.01 mbar); analytically pure colourless oil (136 mg, 68%), solidifying at −7°C; mp 57–58°C, $[\alpha]_D^{20}$ −84.1° (*c* = 1.410, MeOH), containing **19** and **20** in a 94:6 ratio (±) 2; by ^{13}C-NMR); Lit. values for the D-*arabino* compound see *ent*-**19**.

D-*arabino-1,4- and -1,5-Hexonolactones ent*-**19** *and ent*-**20**:

The typical procedure detailed for preparation of **19** is used. L-*erythro*-Triol **1** (125 mg, 1.06 mmol, with $[\alpha]_D^{22}$ −22.9°, see above), $PdCl_2$ (19 mg, 0.11 mmol), $CuCl_2$ (427 mg, 3.18 mmol), NaOAc (260 mg, 3.18 mmol) in AcOH (10 mL); reaction at r.t. for 17 h. Colourless oil that crystallizes on cooling in the refrigerator; 90 mg (59%), mp 57–58°C, bp 140–150°C/0.01 mbar, $[\alpha]_D^{20}$ + 84.3° (*c* = 1.36, MeOH) {Lit.[16]: mp 77–78°C, $[\alpha]_D^{20}$ + 89° (*c* = 1.0, $CHCl_3$)}. The product consists of a 95:5 mixture of 1,4-/1,5-lactones *ent*-**19**/*ent*-**20**; all spectroscopic data in close agreement with those recorded for the compounds **19/20** of the L-series (*vide supra*).

1,4-Anhydro-5-deoxy-L-*lyxo*-hexenitol [(2*S*,3*R*,4*S*)-2-(2-Hydroxyethyl)tetrahydrofuran-3,4-diol, 21]:

A dry (heat-gun) flask is charged with **19** (92:8 – mixture of **19/20**; 100 mg, 0.594 mmol), THF (10 mL), and $LiBH_4$ (63 mg, 2.9 mmol). The mixture is stirred for 2 d at r.t. under N_2, then neutralized with conc. H_2SO_4 (2 drops). The solution, diluted with H_2O (100 mL), is passed through a column (1.8 cm × 8 cm) filled with strongly acidic (Lewatit SPC 118, 12 g), then a like one with medium-basic ion exchange resin (Lewatit MP 64, 12 g). The solutes are concentrated (20 mbar) to afford a yellow oil consisting of **21** with no other diastereomer detectable by ^{13}C-NMR (d.r. > 95:5). Analytically pure **21** (colourless oil) is obtained by filtration of the above oil, dissolved in EtOAc through silica (20 g, column 1.8 cm × 10 cm), followed by drying (P_2O_5, 0.01 mbar). Yield 65 mg (66%), $[\alpha]_D^{23}$ + 9.6° (*c* = 1.295, MeOH).

$C_6H_{12}O_4$ calc. C 48.64 H 8.16
(148.1) found 48.87 8.46

IR (film): *v* = 3340 (br s, OH), 2960, 2880, 1410, 1105, 1005 (all m) cm^{-1}.

3,6-Anhydro-2-deoxy-L-*xylo*-1,4-hexonolactone {(1*S*,5*R*,8*S*)-8-Hydroxy-2,6-dioxabicyclo[3.3.0]octan-3-one} (22) and -L-*lyxo*-1,5-hexonolactone {(1*S*,5*S*,8*S*)-8-Hydroxy-2,6-dioxabicyclo[3.2.1]octan-3-one} (23):
The typical procedure is followed: L-*threo*-triol **7** (157 mg, 1.33 mmol, with $[\alpha]_D^{25}$ −46.2°, see above), $PdCl_2$ (23.1 mg, 0.13 mmol), $CuCl_2$ (536 mg, 3.99 mmol), NaOAc (355 mg, 3.99 mmol) in AcOH (10 mL); reaction at r.t. for 42 h; after Kugelrohr distillation at 130–150 °C (bath temp.)/0.01 mbar and drying (P_2O_5; 0.01 mbar) a yellow oil is obtained that solidifies at −30 °C. Yield 147 mg (77%), 89:11-mixture of **22/23** (from ^{13}C-NMR); $[\alpha]_D^{26}$ +60.5° (*c* = 0.440, MeOH).

Part of this mixture (100 mg) is separated by preparative TLC (silica gel 60 F_{254} 2 mm, E. Merck; eluent EtOAc). Fraction 1: R_f 0.46, colourless solid of **22**, 58 mg, mp 71–73 °C; after recrystallization (*i*-Pr_2O/$CHCl_3$ 1:1, 1.2 mL) colourless crystals, 44 mg, mp 79–81 °C, $[\alpha]_D^{26}$ +77.1° (*c* = 0.265, MeOH) {Lit.[16] mp 84–85 °C, $[\alpha]_D^{20}$ +80° (*c* = 1.07, $CHCl_3$) for **22** obtained from L-gulonolactone}. Fraction 2: R_f 0.31, yellow oil, 40 mg, mixture of **22/23**.

3,6-Anhydro-2-deoxy-D-*gluco*-1,4-heptonolactone {(1*R*,5*S*,7*R*,8*R*)-8-Hydroxy-7-hydroxymethyl-2,6-dioxabicylo[3.3.0]octan-3-one, 24} and 3,7-Anhydro-2-deoxy-D-*gluco*-1,4-heptonolactone **{(1*S*,4*R*,5*R*,6*R*)-4,5-Dihydroxy-2,7-dioxabicyclo[4.3.0]nonan-8-one, 25}**:
According to the typical procedure; D-*lyxo*-hexenitol **12** (1.482 g, 10.0 mmol), $PdCl_2$ (177 mg, 1.00 mmol), $CuCl_2 \cdot 2H_2O$ (5.109 g, 30.0 mmol), NaOAc (2.461 g, 29.96 mmol), AcOH (50 mL); stirring under CO (balloon) at r.t. for 41 h. Crude product after work-up (*vide supra*): yellow oil (3.325 g), purification by chromatography (silica gel, 60 g, column 3 cm × 20 cm, elution with EtOAc); fraction 1 containing the pyrano-lactone **25**, 245 mg (14%), colourless crystals (from MeOH), mp. 135–137 °C, $[\alpha]_D^{20}$ −52.7° (*c* = 0.990, MeOH), R_f 0.39 (EtOAc as eluent); fraction 2 after evaporation and drying (P_2O_5, 0.1 mbar) gives analytically pure **24**, 1.097 g (63%), colourless crystals (from MeOH), mp 49–51 °C, $[\alpha]_D^{20}$ −37.9° (*c* = 0.960, MeOH), R_f 0.25 (EtOAc, as above). In another run, employing anhydrous $CuCl_2$ as usual, 17% of **25** and 60% of **24** were isolated.

^1H-NMR of **25** (DMSO-d_6): δ = 2.26 (d, 1 H, 2-H_n), 2.88 (dd, 1 H, 2-H_x), 3.33–3.51 (m, 2 H, 7-H_a, 7-H_b), 3.55–3.64 (m, 1 H, 6-H), 3.96 (d, 1 H, 5-H), 4.27 (dd, 1 H, 3-H), 4.37 (dd, 1 H, 4-H), 4.92 (d, 1 H, 6-OH), 5.31 (d, 1 H, 5-OH). Coupling constants: $J_{2n,2x}$ = 17.2, $J_{2n,3}$ = 0, $J_{2x,3}$ = 4.5, $J_{3,4}$ = 2.8, $J_{4,5}$ = 3.2, $J_{5,OH}$ = 4.2, $J_{6,OH}$ = 5.9 Hz.

3,6-Anhydro-2-deoxy-L-*ido*-1,4-heptonolactone {(1*R*,5*S*,7*S*,8*R*)-8-Hydroxy-7-hydroxymethyl-2,6-dioxabicyclo[3.3.0]octan-3-one 26}:
In accord with the typical procedure, a 50 mL-flask is charged with D-*xylo*-hexenitol **15** (409 mg, 2.78 mmol), $PdCl_2$ (49 mg, 0.278 mmol), $CuCl_2$ (1.12 g, 8.34 mmol), NaOAc (684 mg, 8.34 mmol), AcOH (10 mL) and stirred under CO (balloon) at r.t. for 48 h (the originally green colour of the mixture turns ochre). The crude product, a yellow oil, is purified by passage through silica gel (20 g, column 1.8 cm × 10 cm; EtOAc), and a colourless, analytically pure solid of **26** is obtained; yield 257 mg (53%), mp 71–72 °C, $[\alpha]_D^{22}$ −23.5° (*c* = 0.950, MeOH), R_f 0.17 (EtOAc).

3,6-Anhydro-2-deoxy-5-*O*-mesyl-L-*ido*-1,4-heptonolactone {(1*R*,5*S*,7*S*,8*R*)-8-Hydroxy-9-hydroxymethyl-2,6-dioxabicyclo-[3.3.0]octan-2-one, 27}:
Following the typical procedure; mesyl-tetrol **18** (434 mg, 1.92 mmol), $PdCl_2$ (34 mg, 0.19 mmol), $CuCl_2$ (774 mg, 5.75 mmol), NaOAc (472 mg, 5.75 mmol), AcOH (10 mL); reaction under CO for 21 h at r.t., until the green colour has turned ochre. The crude product, a yellow oil (666 mg), is chromatographed (silica gel, 20 g, column 1.8 cm × 10 cm; eluent EtOAc); yield of **27** as a yellow oil 327 mg (67%), $[\alpha]_D^{24}$ −28.5° (*c* = 0.880, MeOH), R_f 0.36 (EtOAc).

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(1) Post-doctoral work of Gracza, T., 1988/1991, and part of *Diploma Theses* by Stahl, U. and Hasenöhrl, T., Würzburg 1989/1991. The preparation of D-*lyxo*-hexenitol **12** is taken from Häfele, B. *Dissertation*, Würzburg 1987. Preliminary results were presented in lectures, e.g. at Münster (Jan. 1989), Rhône-Poulenc/Lyon (March 1989), Orléans (Jan. 1991), and in poster form:
Gracza, T.; Hümmer, W.; Jäger, V. *Proceedings 10th Symposium on the Chemistry of Heterocyclic Compounds*, Kosice/CSFR, Aug. 13–17, 1990, p. 34.

(2) Schaffner, R., in *The Carbohydrates*, 2nd Ed., Vol. IA, Pigman, W.; Horton, D. (eds.), Academic Press, New York, 1972, p. 69.
Carbohydrates, Collins, D.M. (ed.), Munasinghe, V.R.N. (principal contributor), Chapman and Hall, London, New York, 1987.
Glasby, J. *Encyclopaedia of Antibiotics*, 2nd Ed., J. Wiley, Chichester, 1979.
Secrist, J.A.; III; Barnes, K.D.; Wu, S.-R., in: *Trends in Carbohydrate Chemistry*, Horton, D.; Hawkins, L.D.; McGarvey, G.J. (eds.), ACS Symposium Series No. 386, A.C.S., Washington, D.C., 1989, p. 93.

(3) Vasella, A., in: *Modern Synthetic Methods*, Vol. 2, Scheffold, R. (ed.), Salle & Sauerländer, Frankfurt, 1980, p. 173.
Hanessian, S. *Total Synthesis of Natural Products: The 'Chiron' Approach*, Pergamon Press, Oxford, 1983.

(4) Hanessian, S.; Pernet, A.G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111.
Mizuno, Y. *Studies in Organic Chemistry, 24, The Organic Chemistry of Nucleic Acids*, Kodansha Ltd., Tokyo & Elsevier, Amsterdam, 1987, pp. 72.

(5) Martin, O.R.; Lai, W. *J. Org. Chem.* **1990**, *55*, 5188, and references therein.

(6) Bartlett, P.A., in: *Selectivity – A Goal for Synthetic Efficiency*, Bartmann, W.; Trost, B.M. (eds.), Verlag Chemie, Weinheim, 1984, p. 1.
Boivin, T.L.B. *Tetrahedron* **1987**, *43*, 3309.

(7) Many examples may be found in Ref. 2–4. A selection of further work is given in the following references.

(8) *C*-Glycosidic structures from Wittig reactions:
Ohrui, H.; Jones, G.H.; Moffatt, J.G.; Maddox, M.L.; Christensen, A.T.; Byram, S.K. *J. Am. Chem. Soc.* **1975**, *97*, 4602.
Tronchet, J.M.J.; Gentile, B. *Helv. Chim. Acta* **1979**, *62*, 2091.
Reed, L.A.; III; Ito, Y.; Masamune, S.; Sharpless, K.B. *J. Am. Chem. Soc.* **1982**, *104*, 6468.
Fraser-Reid, B.; Tam, T.F.; Sun, K.M., in: *Organic Synthesis Today and Tomorrow*, Trost, B.M.; Hutchinson, C.R. (eds.), Pergamon Press, Oxford, 1981, p. 319.
Maryanoff, B.E.; Reitz, A.B. *Chem. Rev.* **1989**, *89*, 863.

(9) *C*-Glycosyl structures from vinyl, allyl and furyl metal derivatives, see, for example:
Boschetti, A.; Nicotra, F.; Panza, L.; Russo, G. *J. Org. Chem.* **1988**, *53*, 4181.
Lewis, M.D.; Cha, J.K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976.
Achmatowicz, O., in: *Organic Synthesis Today and Tomorrow*, Trost, B.M.; Hutchinson, C.R. (eds.), Pergamon Press, Oxford, 1981, p. 307.
Casiraghi, G.; Colombo, L.; Rassu, G.; Spanu, P. *J. Org. Chem.* **1990**, *55*, 2565.

(10) *C*-Homologation via 2-oxoglycosyl bromides:
Lichtenthaler, F.W.; Schwidetzky, S.; Nakamura, K. *Tetrahedron Lett.* **1990**, *31*, 71.
(11) Via glycosyl radical C,C-bond formation:
Giese, B.; Linker, T.; Muhn, R. *Tetrahedron* **1989**, *45*, 935.
(12) Pd-catalyzed reactions forming *C*-glycosides/-nucleosides:
Hacksell, U.; Daves, G.D., Jr. *J. Org. Chem.* **1983**, *48*, 2871.
RajanBabu, T. *J. Org. Chem.* **1985**, *50*, 3642.
(13) Use of glycosyl manganese derivatives:
DeShong, P.; Slough, G.A.; Elango, V. *J. Am. Chem. Soc.* **1985**, *107*, 7788.
DeShong, P.; Slough, G.A.; Elango, V. *Carbohydr. Res.* **1987**, *171*, 342.
(14) See for example Ref. 3, 4, 8 (Ohrui).
(15) Syntheses from furan and respective use of racemic 3,6-anhydro-2-deoxy-*allo*-heptonolactones:
Gensler, W.J.; Chan, S.; Ball, D.B. *J. Am. Chem. Soc.* **1975**, *97*, 436.
Further uses, after optical resolution:
Sato, T.; Ho, R.; Hayakawa, Y.; Noyori, R. *Tetrahedron Lett.* **1978**, 1829.
Noyori, R.; Sato, T.; Hayakawa, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2561.
(16) L-*xylo*- and D-*arabino*-3,6-anhydro-2-deoxy-hexonolactones **22** and **19** from L-gulono- and D-mannonolactone:
Vekemans, J.A.J.M.; Dapperens, C.W.M.; Claessen, R.; Koten, A.M.J.; Godefroi, E.F.; Chittenden, G.J.F. *J. Org. Chem.* **1990**, *55*, 5336.
(17) Synthesis of precursors:
Bock, K.; Lundt, I.; Pedersen, C. *Carbohydr. Res.* **1981**, *90*, 7.
(18) Cf. 3,6-anhydro-L-gulono- and -idono-lactones:
Heyns, K.; Linkies, A. *Chem. Ber.* **1968**, *101*, 4199, 4209;
Heyns, K.; Linkies, A. *Ibid.* **1975**, *108*, 3633.
(19) Tamaru, Y.; Kobayashi, T.; Kawamura, S.-i.; Ochiai, H.; Hojo, M.; Yoshida, Z.-i. *Tetrahedron Lett.* **1985**, *26*, 3207.
(20) Tamaru, Y.; Hojo, M.; Yoshida, Z.-i. *J. Org. Chem.* **1991**, *56*, 1099.
(21) Semmelhack, M.F.; Bodurow, C. *J. Am. Chem. Soc.* **1984**, *106*, 1496.
Cf.: Holmes, C.P.; Bartlett, P.A. *J. Org. Chem.* **1989**, *54*, 98.
(22) Semmelhack, M.F.; Zhang, N. *J. Org. Chem.* **1989**, *54*, 4483.
See also:
McCormick, M.; Monahan, R., III; Soria, J.; Goldsmith, D.; Liotta, D. *J. Org. Chem.* **1989**, *54*, 4485.
(23) Semmelhack, M.F.; Bodurow, C.; Baum, M. *Tetrahedron Lett.* **1984**, *25*, 3171.
For a review see:
Semmelhack, M.F.; Kim, C.; Zhang, N.; Bodurow, C.; Sanner, M.; Dobler, W.; Meier, M. *Pure Appl. Chem.* **1990**, *62*, 2035.
(24) For reviews on Pd(II)-mediated chemistry see:
Collman, J.P.; Hegedus, L.S.; Norton, J.R.; Finke, R.G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books/Oxford University Press, Mill Valley, CA, 1987.
Hegedus, L.S. *Tetrahedron* **1984**, *40*, 2415.
Trost, B.M. *Tetrahedron* **1977**, *33*, 2615.
Heck, R.F. *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1990, p.381.
(25) For other transition metal-provoked carbonylations of carbohydrate substrates with Co-, Fe-, Mn-carbonyl complexes see:
Rosenthal, A.; Kan, G. *Tetrahedron Lett.* **1967**, 477 (Co).
Rosenthal, A. *Adv. Carbohydr. Chem. Biochem.* **1968**, *23*, 59.
Baer, H.H.; Hanna, H.R. *Carbohydr. Res.* **1982**, *102*, 169 (Fe).
Ref. 13 (Mn) and references cited therein.
(26) For an authoritative review on these and other cyclofunctionalizations see:
Cardillo, G.; Orena, M. *Tetrahedron* **1990**, *46*, 3321.
(27) For related intramolecular amidocarbonylations see:
Tamaru, Y.; Kobayashi, T.; Kawamura, S.-i.; Ochiai, H.; Yoshida, Z.-i. *Tetrahedron Lett.* **1985**, *26*, 4479.
Tamaru, Y.; Hojo, M.; Yoshida, Z.-i. *J. Org. Chem.* **1988**, *53*, 5731.
Lathbury, D.; Vernon, P.; Gallagher, T. *Tetrahedron Lett.* **1986**, *27*, 6009.
See also Ref. 24 and 28.
(28) Jäger, V.; Hümmer, W. *Angew. Chem.* **1990**, *102*, 1182; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1171.
(29) In yet another variant, allylic and other unsaturated alcohols are converted to lactones by hydro-carbonylation:
El Ali, B.; Alper, H. *J. Org. Chem.* **1991**, *56*, 5357.
Alper, H. *Aldrichimica Acta* **1991**, *24*, 3, and earlier papers cited therein.
(30) Jäger, V.; Müller, I.; Schohe, R.; Frey, M.; Ehrler, R.; Häfele, B.; Schröter, D. *Lect. Heterocycl. Chem.* **1985**, *8*, 79.
Jäger, V.; Häfele, B.; Schröter, D. *Angew. Chem.* **1986**, *98*, 89; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 87.
Koppenhoefer, B.; Walser, M.; Schröter, D.; Häfele, B.; Jäger, V. *Tetrahedron* **1987**, *43*, 2059.
Cf. also Hatakeyama, S.; Sakurai, K.; Takano, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1759.
(31) Jäger, V.; Häfele, B. *Synthesis* **1987**, 801.
(32) Jäger, V.; Schröter, D.; Koppenhoefer, B. *Tetrahedron* **1991**, *47*, 2195.
(33) Jäger, V.; Franz, R.; Schwab, W.; Häfele, B.; Schröter, D.; Schäfer, D.; Hümmer, W.; Guntrum, E.; Seidel, B. in: *Studies in Organic Chemistry*, Vol. 35, Kovác, J.; Zálupsky, P. (eds.), Elsevier, Amsterdam, 1988, p. 58.
(34) Hümmer, W.; Gracza, T.; Jäger, V. *Tetrahedron Lett.* **1989**, *30*, 1517.
Jäger, V.; Hümmer, W.; Stahl, U.; Gracza, T. *Synthesis* **1991**, 769.
(35) Jäger, V.; Stahl, U.; Hümmer, W. *Synthesis* **1991**, 776.
(36) Trost, B.M.; Angle, S.R. *J. Am. Chem. Soc.* **1985**, *107*, 6123.
Wershofen, S.; Scharf, H.-D. *Synthesis* **1988**, 854.
(37) Myers, A.G.; Widdowson, K.L. *Tetrahedron Lett.* **1988**, *29*, 6389.
Cf. McCombie, S.W.; Metz, W.A. *Tetrahedron Lett.* **1987**, *28*, 383.
(38) Corey, E.J.; Hopkins, P.B.; Munroe, J.E.; Marfat, A.; Hashimoto, S.-i. *J. Am. Chem. Soc.* **1980**, *102*, 7986.
Cf. Minami, N.; Ko, S.S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109.
(39) Roush, W.R.; Brown, R.J. *J. Org. Chem.* **1982**, *47*, 1371.
Roush, W.R.; Brown, R.J. *Ibid.* **1983**, *48*, 5093.
Roush, W.R.; Brown, R.J.; DiMare, M. *J. Org. Chem.* **1983**, *48*, 5083.
Cf. Katsuki, T.; Lee, A.W.M.; Ma, P.; Martin, V.S.; Masamune, S.; Sharpless, K.B.; Tuddenham, D.; Walker, F.J. *J. Org. Chem.* **1982**, *47*, 1378.
(40) Bladon, P.; Owen, L.N. *J. Chem. Soc.* **1950**, *591*, 598.
(41) Hall, L.D.; Hough, L.; Pritchard, R.A. *J. Chem. Soc.* **1961**, 1537.
(42) Jones, J.K.N.; Thompson, J.L. *Can. J. Chem.* **1957**, *35*, 955.
(43) Häfele, B. *Dissertation*, Univ. Würzburg, 1987, pp. 89, 189.
(44) Wolfrom, M.L.; Wood, H.B., Jr. *J. Am. Chem. Soc.* **1951**, *73*, 2933.
Wolfrom, M.L.; Wood, H.B.; Jr. *Ibid.* **1952**, *74*, 5583.
Abdel-Akker, M.; Hamilton, J.K.; Smith, F. *J. Am. Chem. Soc.* **1951**, *73*, 4691.
(45) Karrer, P.; Davis, P.C. *Helv. Chim. Acta* **1948**, *31*, 1611.
(46) See, for example:
Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1979**, *62*, 1990.
Inch, T.D. *Tetrahedron* **1984**, *40*, 3161.
(47) Baird, W.C., Jr. *J. Org. Chem.* **1966**, *31*, 2411.
Baker, R.; Halliday, D.E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 208.
Stille, J.K.; James, D.E. *J. Am. Chem. Soc.* **1975**, *97*, 674.
James, D.E.; Hines, L.F.; Stille, J.K. *J. Am. Chem. Soc.* **1976**, *98*, 1806.
James, D.E.; Stille, J.K. *J. Am. Chem. Soc.* **1976**, *98*, 1810.
Stille, J.K.; Divakuruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303.
Giddings, R.M.; Whittaker, D. *Tetrahedron Lett.* **1978**, 4077.
Heumann, A.; Waegell, B. *Nouv. J. Chim.* **1977**, *1*, 277.
Heumann, A.; Reglier, M.; Waegell, B. *Angew. Chem.* **1979**, *91*, 924, 925; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 866.

(48) Cf., for example: Jäger, V.; Müller, I. *Tetrahedron* **1985**, *41*, 3519.
(49) Fang, X.-p.; Anderson, J.E.; Chang, C.-j.; Fanwick, P.E.; McLaughlin, J.L. *J. Chem. Soc., Perkin Trans 1* **1990**, 1655.
(50) A beautiful collection of carbohydrate ^{13}C-NMR data is presented by:
Bock, K.; Pedersen, C. *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 27.
(51) Takano, S.; Iwabuchi, Y.; Ogasawara, K. *J. Am. Chem. Soc.* **1991**, *113*, 2786.
(52) Miginiac, P. *Ann. Chem.* **1962**, *7*, 445; see also Ref. 32.
(53) Wiggins, L.F. *J. Chem. Soc.* **1946**, 3.
(54) Ohle, H.; Dickhauser, E. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 2593.
(55) Shyluk, W.P.; Honeyman, J.; Timell, T.E. *Can. J. Chem.* **1955**, *33*, 1202.